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# The onset of particle agglomeration during the dry ultrafine grinding of limestone in a planetary ball mill

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ABSTRACT

This study investigates structural and morphological changes in limestone particles ground in a planetary ball mill. The grinding tests were carried out as a function of the revolution speed (100–300 rpm) and time (7–120 min). The feed size, the grinding media and the filling rate were kept constant. The size and shape of the particles were characterized by laser scattering and scanning electron microscopy (SEM), respectively. The uniformity index given by the Rosin–Rammler particle size distribution combined with SEM micrographs was useful to show the decrease of the grinding rate caused by the agglomeration of fines lying on partially broken particles. The effect of the mechanical action of grinding on the crystalline structure of calcite grains was investigated by X-ray diffraction (XRD) and electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy was performed before and after the samples being irradiated with a dose of 5 kGy of gamma rays. XRD analysis only showed a net reduction in the intensity of the $(10\bar{1}4)$ peak and a slight increase in the line broadening of this peak. On the other hand, the energy input provided by the grinding action modified the population of paramagnetic defects existing in calcite lattice. In addition to the creation of electron traps responsible for a signal with a g-factor equal to 1.9999, the EPR measurements showed that the intensity of the hyperfine lines of $Mn^{2+}$ substituting $Ca^{2+}$ was affected by the grinding action. The morphological and particle size analysis together with the relationship found between the intensity of paramagnetic defects and specific surface area of limestone particles provided a picture of the onset of the agglomeration process. These results were discussed in order to explain the apparent grinding limit observed in ultrafine milling of limestone.



## 1. Introduction

The size reduction of particulate materials below 10 μm by high-energy milling is known as ultrafine grinding. The ultrafine grinding occurs in different types of high energy mills, which the most common are vibratory, planetary, air-jet and stirred media mills [1,2]. In mineral processing, the main application of high-energy milling is size reduction of industrial minerals such as quartz and quartzite, feldspars, carbonate rocks, kaolinite and gypsum. Ultrafine powders have numerous applications in the manufacturing of ceramics, chemical and pharmaceutics products, paper making industries, etc. [3]. The manufacturing of ultrafine powders may occur in wet or dry grinding conditions. The usage of dispersants in wet processes reduces the effect of interparticle interactions and decreases the possibility to create alterations in the mineral structure such as lattice distortions, lattice strains, reduction in crystallite size and amorphization. Nevertheless, in industrial manufacturing processes, the wet grinding is frequently followed by solid–liquid phase separation and drying which entails several practical difficulties and losses inherent to handling ultrafine particles [4,5]. Due to these problems alternative methods for dry ultrafine grinding of industrial minerals are a significant issue. These issues pertain to a better understanding of structural modifications caused by the thermo-mechanical action of dry grinding on the particulate material.

The manufacturing of ultrafine powders is influenced by two counteracting processes: particle breakage and interparticle interaction [6–8]. Particle breakage is dependent on microcracking propagation controlled on the most basic level by the Griffith criterion of brittle fracture [9]. It affects the kinetics of the comminution processes and increases the specific surface area of the grinding product. Interparticle interactions are governed by interfacial and surface properties such as intermolecular forces and chemical reactivity. It controls the kinetics of aggregation during the comminution operation and reduces the specific surface area of the grinding product. For a long time, aggregation and agglomeration mechanisms resultant from interparticle interactions have been attributed to van der Waals forces, polar interactions and strong chemical forces [6,8]. However, specific crystalline distortions and/or surface defects responsible for interfacial forces existing between ultrafine particles have not been properly

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characterized until now. In this context, electron paramagnetic resonance (EPR) spectroscopy emerges as an attractive analytical issue because it is a powerful technique to investigate short-range lattice imperfections having unpaired electron spins, i.e., paramagnetic centers associated with ions or point defects [10]. Although EPR spectroscopy has been used successfully in the characterization of radicals induced in polymers by mechanical action, only a few studies have adopted magnetic resonance methods to investigate lattice defects created by high-energy milling in particulate solids [11–13]. In this study, EPR spectroscopy was further used to investigate the creation of defect centers in the calcite structure of limestone induced by high-energy milling.

For a long time, powder X ray diffraction (XRD) has been the most popular analytical tool to investigate structural changes in particulate minerals induced by ultrafine grinding [14–18]. Coupled with scanning electron microscopy (SEM) and particle size analysis, the measurement of the broadening of the diffracting profiles has been useful to investigate the agglomeration of ultrafine particles in the nanometer range [19,20]. Measuring the crystallite size and the lattice strain by line profile analysis, Knieke et al. [19] succeeded in characterizing the true limit of grinding in zirconia nanoparticles. These authors showed that the true grinding limit was reached when the crystallites became so small that no defects can be stored in the crystalline lattice. However, the nature of lattice defects created in zirconia structure by high-energy milling remains unknown. Similarly, XRD line broadening analysis coupled with SEM and infrared (IR) spectroscopy carried out by Li et al. [20] was useful to characterize agglomeration and polymorphic transformation in calcite nanoparticles induced by dry ultrafine grinding but the nature of the defects responsible for the agglomeration is unknown.

The technological importance of exploring structural changes and aggregation mechanisms induced by high-energy milling in particulate materials arises from the fact that certain properties of the grinding product such as the ability to hydrate, reactivity and solubility are negatively affected. Thus, the aim of this study was to identify the beginning of the cohesive attraction between ground particles of limestone and to characterize modifications in the crystalline structure of calcite induced by the mechanical action of the dry grinding in a planetary ball mill. For this study, the onset of the aggregation between particles was characterized by combining dimensional and morphological analysis of the particulate state. The structural changes were investigated by means of the measurement of the intensity and the broadening of diffracting peaks of calcite and the evaluation of the EPR signal of the hyperfine structure of $Mn^{2+}$ centers as well as the creation of superficial electron deficient centers as a function of the grinding conditions. Particle size parameters and EPR signal intensities were correlated to each other in order to examine the origin of the cohesive attraction between ultrafine particles of limestone.

## 2. Experimental

This study was carried out with metamorphic limestone blocks taken from Currais Novos district (Rio Grande do Norte, Brazil). The result of the X-ray fluorescence spectrometry showed that its major constituents are calcite (76%) and dolomite (16%). The samples measured in this study belong to the same batch of material ground in our previous study in which sample preparation procedures and grinding experiments were described in detail [13]. The essentials of this methodology can be summarized as follows. Aliquots of 40 ml (~60 g) with mean particle size equal to 113 μm were ground in a *Fritsch Pulverisette 5* planetary mill with tempered tool-steel bowls (inner diameter: 75 mm; volume: 250 ml) and 40 balls of 10 mm diameter (21 ml). The experiments were carried out with different revolution speeds (100, 150, 200 and 300 rpm) varying the grinding periods from 7 to 120 min. For grinding times ≥60 min, a break of 5 min was adopted after each 30 min of grinding followed by the reversal of the direction of the revolution. All tests were carried out in dry with the bowls rotating in the counter direction against the revolution disc. Considerable aggregation of limestone particles on the surfaces of balls and bowls occurred for grinding time ≥60 min with 200 rpm and ≥15 min with 300 rpm. The disaggregation was made manually and this procedure affected the dimensions of large-sized agglomerates in the ground product.

The particle size distributions were measured by using a laser granulometer model *Malvern Matersizer 2000*. The measurements were carried out in water using the Hydro 2000 accessory. Each sample was measured three times with different aliquots and each (dispersed) aliquot was read three times. The nominal diameters $d_{10}$, $d_{50}$ and $d_{90}$ were calculated averaging the mean values of each measurement. The nominal diameters $d_{10}$, $d_{50}$ and $d_{90}$, correspond to the apertures related to 10, 50 and 90% of passing material, respectively. The specific surface area ($S$) of each size distribution was calculated by the equipment, as follows: $S = (6/\rho)D[3,2]$, where $D[3,2]$ is the surface weighted mean diameter and ρ is the specific mass of calcite (2.72 g/cm$^3$). The particle morphology was analyzed by scanning electron microscopy (SEM) using the *JEOL JSM-6460* microscope. The images were obtained with secondary (SE) electrons in vacuum with 30 kV. The particles were coated with a gold layer. The analyses were carried out with magnifications varying from 100 to 4000 ×.

The effect of the grinding conditions on the crystalline structure of the limestone was initially analyzed by X-ray powder diffraction (XRD). To reduce the effect of preferential orientation during sample preparation, the samples were filled into a back-loading sample-holder. The XRD patterns were obtained with a *Bruker D2-Phaser* diffractometer equipped with a *Lynxeye* one-dimensional detector; Cu-Kα radiation (30 kV, 10 mA; $K\alpha_1$ wavelength: 1.54060 Å); goniometer step of 0.02020°/s; counting time 1 s and 2θ scanning from 4° to 80°. The diffracting peaks were indexed by using the *Bruker-AXS Diffrac.Eva* software and the COD 2011 database. Besides calcite and dolomite, the presence of biotite, clinochlore, edenite, kaolinite and talc was identified. The full-width at half-maximum (FWHM) was adopted to evaluate the peak line broadening [17,21]. For this, the XRD patterns were obtained with 2θ scanning from 22° to 32° and counting time of 3 s. In order to evaluate the experimental uncertainty, the procedure (sample filling into the sample-holder and acquisition of XRD pattern) was repeated three times for several samples. The intensity and the FWHM of $(01\bar{1}2)$, $(10\bar{1}4)$ and (0006) diffracting peaks of calcite were measured with the aid of the *Bruker-AXS Diffrac.Eva* software after removing the background and the contribution of the $K\alpha_2$ radiation.

The structural changes induced by grinding were also investigated by electron paramagnetic resonance (EPR) spectroscopy in aliquots of 100 mg placed into fused quartz tubes with inner diameter equal to 3 mm. These measurements were carried out in a *Bruker EMX 10-Plus* spectrometer operating at the X-band (~9.83 GHz) provided with a high sensitive cylindrical cavity. Initially, the magnetic field was swept from 1000 to 5500 G. For specific magnetic field intervals, the signal was recorded as a function of the microwave power ranging from 0.02 to 20 mW. Then, the EPR intensity was recorded at room temperature by sweeping the magnetic field from 3400 to 3550 G setting the parameters as follows: microwave power: 2 mW; modulation amplitude of the magnetic field: 2.5 and 1 G; modulation frequency: 100 kHz; time constant: 5.12 ms; conversion time: 25 ms; receiver gain: $5 \times 10^2$; and number of scans: 5. The calibration of the magnetic field and the sensitivity of the spectrometer were regularly checked with a DPPH standard. The signal intensities were quantified by peak-to-peak measurements in the first-derivative of the EPR spectra. The EPR spectra were obtained before and after the samples had been irradiated with a dose of 5 kGy of γ rays. The irradiation was carried out in a γ-cell irradiator ($^{60}$Co) with a dose rate of 3.50 kGy/h approximately. The samples were measured again several months after irradiation in order to check the stability of the EPR signals.